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(54) METHOD AND APPARATUS FOR FORMING A COATING

VERFAHREN UND VORRICHTUNG ZUR HERSTELLUNG EINER BESCHICHTUNG

PROCEDE ET APPAREIL POUR FORMER UN REVETEMENT

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Description

[0001] The present invention relates to a method for forming a coating on a substrate, in particular a method for forming a coating on a substrate using an atmospheric pressure plasma discharge, a method for polymerising a polymer forming material, and further to apparatus for forming a coating on a substrate.

[0002] Substrates may be coated for a variety of reasons, for example to protect the substrate from corrosion, to provide a barrier to oxidation, to improve adhesion with other materials, to increase surface activity, and for reasons of biomedical compatibility of the substrate. A commonly used method for modifying or coating the surface of a substrate is to place the substrate within a reactor vessel and subject it to a plasma discharge. Many examples of such treatment are known in the art; for example, US patent number 5,876,753 discloses a process for attaching target materials to a solid surface which process includes affixing carbonaceous compounds to a surface by low power variable duty cycle pulsed plasma deposition, and EP-A-0896035 discloses a device having a substrate and a coating, wherein the coating is applied to the substrate by plasma polymerisation of a gas comprising at least one organic compound or monomer. DE 19924108, which was first published after the initial priority date of the present application, describes a process for coating dyestuffs and corrosion inhibitors onto substrates. The process involves the application of a liquid film coating onto a substrate and a subsequent plasma polymer protective coating. The plasma polymer coating is formed using gaseous monomers and low pressure plasma.

[0003] However, such plasma surface treatments require the substrate to be under conditions of reduced pressure, and hence require a vacuum chamber. Typical coating-forming gas pressures are in the range 5 to 25 Nm⁻² (cf. 1 atmosphere = 1.01x10⁵ Nm⁻²). As a result of the requirement for reduced pressure, surface treatments are expensive, are limited to batch treatments, and the coating-forming materials must be in gaseous and/or vapour form in order to maintain conditions of reduced pressure.

[0004] The present inventors have found that the abovementioned disadvantages of substrate surface plasma treatment can be overcome using a combination of an atmospheric pressure plasma discharge and an atomised liquid and/or solid coating forming material.

[0005] Thus, according to the present invention there is provided a method for forming a coating on a substrate, which method comprises introducing an atomised liquid and/or solid coating-forming material into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom, and exposing the substrate to the atomised coating-forming material.

[0006] It is to be understood that the coating forming material in accordance with the present invention is a material which can be used to make any appropriate coating, including, for example, a material which can be used to grow a film or to chemically modify an existing surface.

[0007] The present invention also provides a method for polymerising a polymer-forming material, which method comprises atomising the polymer-forming material, and exposing the polymer-forming material to an atmospheric pressure plasma discharge.

[0008] The present invention further provides apparatus for forming a coating on a substrate, which apparatus comprises means for generating an atmospheric pressure plasma discharge within which, in use, the substrate is placed, an atomiser for providing an atomised coating-forming material within the plasma discharge, and means for supplying a coating forming material to the atomiser.

[0009] Any conventional means for generating an atmospheric pressure plasma glow discharge may be used in the present invention, for example atmospheric pressure plasma jet, atmospheric pressure microwave glow discharge and atmospheric pressure glow discharge. Typically such means will employ a helium diluents and a high frequency (e.g. > 1 kHz) power supply to generate a homogeneous glow discharge at atmospheric pressure via a Penning ionisation mechanism, (see for example, Kanazawa et al, J.Phys. D: Appl. Phys. 1988, 21, 838, Okazaki et al, Proc. Jpn. Symp. Plasma Chem. 1989, 2, 95, Kanazawa et al, Nuclear Instruments and Methods in Physical Research 1989, B37/38, 842, and Yokoyama et al., J. Phys. D: Appl. Phys. 1990, 23, 374).

[0010] The coating-forming material may be atomised using any conventional means, for example an ultrasonic nozzle. The atomiser preferably produces a coating-forming material drop size of from 10 to 100 µm, more preferably from 10 to 50 µm. Suitable atomisers for use in the present invention are ultrasonic nozzles from Sono-Tek Corporation, Milton, New York, USA. The apparatus of the present invention may include a plurality of atomisers, which may be of particular utility, for example, where the apparatus is to be used to form a copolymer coating on a substrate from two different coating-forming materials, where the monomers are immiscible or are in different phases, e.g. the first is a solid and the second is gaseous or liquid.

[0011] The present invention may be used to form many different types of substrate coatings. The type of coating which is formed on the substrate is determined by the coating-forming material(s) used, and the present method may be used to (co)polymerise coating-forming monomer material(s) onto the substrate surface. The coating-forming material may be organic or inorganic, solid and/or liquid. Suitable organic coating-forming materials include carboxylates, methacrylates, acrylates, styrenes, methacrylonitriles, alkenes and dienes, for example methyl methacrylate, ethyl

methacrylate, propyl methacrylate, butyl methacrylate, and other alkyl methacrylates, and the corresponding acrylates, including organofunctional methacrylates and acrylates, including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates, and fluoroalkyl (meth)acrylates, methacrylic acid, acrylic acid, fumaric acid and esters, itaconic acid (and esters), maleic anhydride, styrene, α -methylstyrene, halogenated alkenes, for example, vinyl halides, such as vinyl chlorides and vinyl fluorides, and fluorinated alkenes, for example perfluoroalkenes, acrylonitrile, methacrylonitrile, ethylene, propylene, allyl amine, vinylidene halides, butadienes, acrylamide, such as N-isopropylacrylamide, methacrylamide, epoxy compounds, for example glycidoxypolytrimethoxysilane, glycidol, styrene oxide, butadiene monoxide, ethyleneglycol diglycidylether, glycidyl methacrylate, bisphenol A diglycidylether (and its oligomers), vinylcyclohexene oxide, conducting polymers such as pyrrole and thiophene and their derivatives, and phosphorus-containing compounds, for example dimethylallylphosphonate. Suitable inorganic coating-forming materials include metals and metal oxides, including colloidal metals. Organometallic compounds may also be suitable coating-forming materials, including metal alkoxides such as titanates, tin alkoxides, zirconates and alkoxides of germanium and erbium. However, the present inventors have found that the present invention has particular utility in providing substrates with silica- or siloxane-based coatings using coating-forming compositions comprising silicon-containing materials. Suitable silicon-containing materials for use in the method of the present invention include silanes (for example, silane, alkylsilanes, alkoxysilanes) and linear (for example, polydimethylsiloxane) and cyclic siloxanes (for example, octamethylcyclotetrasiloxane), including organo-functional linear and cyclic siloxanes (for example, Si-H containing, halo-functional, and haloalkyl-functional linear and cyclic siloxanes, e.g. tetramethylcyclotetrasiloxane and tri(nonofluorobutyl)trimethylcyclotrisiloxane). A mixture of different silicon-containing materials may be used, for example to tailor the physical properties of the substrate coating for a specified need (e.g. thermal properties, optical properties, such as refractive index, and viscoelastic properties).

[0012] In addition, under oxidising conditions the present method may be used to form an oxygen containing coating on the substrate. For example, silica-based coatings can be formed on the substrate surface from atomised silicon-containing coating-forming materials. Under reducing conditions, the present method may be used to form oxygen free coatings, for example, silicon carbide based coatings may be formed from atomised silicon containing coating forming materials.

[0013] Plasma generating conditions containing gases other than oxygen may also be employed, for example noble gases, air, hydrogen, nitrogen and ammonia. In a nitrogen containing atmosphere nitrogen can bind to the substrate surface, and in an atmosphere containing both nitrogen and oxygen, nitrates can bind to and/or form on the substrate surface. Such gases may also be used to pre-treat the substrate surface prior to exposure to the coating forming substance. For example oxygen containing plasma treatment of the substrate may provide improved adhesion with the applied coating. The oxygen containing plasma being generated by introducing oxygen containing materials to the plasma such as oxygen gas or water. Furthermore, the coating formed on the substrate may be post treated in a range of plasma conditions. For example, siloxane derived coatings may be further oxidised by oxygen containing plasma treatment. The oxygen containing plasma being generated by introducing oxygen containing materials to the plasma such as oxygen gas or water.

[0014] An advantage of the present invention over the prior art is that both liquid and solid atomised coating-forming materials may be used to form substrate coatings, due to the method of the present invention taking place under conditions of atmospheric pressure. Furthermore the coating-forming materials can be introduced into the plasma discharge or resulting stream in the absence of a carrier gas, i.e. they can be introduced directly by, for example, direct injection, whereby the coating forming materials are injected directly into the plasma.

[0015] As mentioned above, the present inventors have found particular utility of the present invention for forming silica- and siloxane-based coatings on substrates using silicon-containing materials. Under oxidising conditions, e.g. an oxygen containing atmosphere, silica-based coatings can be formed on the substrate surface from atomised silicon-containing materials, whereas under non-oxidising conditions a siloxane polymer, e.g. a linear, branched or resinous siloxane polymer, can be formed on the substrate surface from atomisation of a silicon-containing monomer. A siloxane-organic copolymer can be formed on the substrate surface by use of a mixture of organic and silicon-containing monomers. Furthermore, a silica-based coating may be formed on a substrate surface, which may in turn be coated by a further material, for example an organic or siloxane polymer. For example, when a siloxane is mixed with an organic polymer and a substrate formed from said mixture, the siloxane will migrate to the surface of the organic polymeric body of the substrate, due to the difference in surface energy between organic polymers and siloxanes. If this substrate is then subjected to atmospheric pressure plasma treatment, the siloxane on the surface of the substrate is oxidised to form a silica-based coating. This silica-based coating may then be subjected to treatment according to the present invention, by further subjecting it to atmospheric pressure plasma treatment in the presence of atomised silicon-containing monomers, to form a siloxane coating thereon. However, the present invention is also useful for forming an organic coating on a substrate, for example a polyacrylic acid or perfluoro-organic coating.

[0016] The substrate to be coated may comprise any material, for example metal, ceramic, plastics, siloxane, woven

or non-woven fibres, natural fibres, synthetic fibres, cellulosic material and powder. However, the size of the substrate is limited by the dimensions of the volume within which the atmospheric pressure plasma discharge is generated, i.e. the distance between the electrodes of the means for generating the plasma. For typical plasma generating apparatus, the plasma is generated within a gap of from 5 to 50mm, for example 12 to 25mm. Thus, the present invention has particular utility for coating films, fibres and powders.

[0017] Substrates coated by the method of the present invention may have various utilities. For example, a silica-based coating, generated in an oxidising atmosphere, may enhance the barrier and/or diffusion properties of the substrate, and may enhance the ability of additional materials to adhere to the substrate surface; a halo-functional organic or siloxane coating (e.g. perfluoroalkenes) may increase hydrophobicity, oleophobicity, fuel and soil resistance, and/or the release properties of the substrate; a polydimethylsiloxane coating may enhance water resistance and release properties of the substrate, and may enhance the softness of fabrics to touch; a polyacrylic acid polymeric coating may be used as an adhesive layer to promote adhesion to substrate surface or as part of laminated structure; the inclusion of colloidal metal species in the coatings may provide surface conductivity to the substrate, or enhance its optical properties. Polythiophene and polypyrrole give electrically conductive polymeric coatings which may also provide corrosion resistance on metallic substrates.

[0018] One major problem which tends to occur when coating substrates using a process involving plasma treatment is that the chemical properties of the material used to form the coating may be lost. It is therefore a major advantage of the present invention that the chemical properties of the coating forming material are substantially retained in the coating formed. For example, in the case where acrylic acid is used as the coating forming material, the carboxylic acid functionality is substantially maintained in the coating formed.

[0019] The present invention also provides a method of producing a substrate having a multi-layered coating by the above described processes. In this case a layer of the coating is applied upon each repeat pass of the substrate through the atmospheric plasma glow discharge. Preferably in such a case the substrate may be coated on a continuous basis by being transported through an atmospheric plasma glow discharge by way of a reel to reel process in which the substrate travels from a first reel, through the glow discharge and on to a second reel at a constant speed to ensure that all the substrate has a predetermined residence time within the glow discharge. Each substrate may be subjected to one or more passes through the glow discharge whereby the first or supply reel in the first pass becomes the substrate collecting reel in the second pass and the substrate collecting reel of the first pass in turn is the supply reel in the second pass, the two reels changing over at the end of each pass. Alternatively the substrate may be passed through a series of atmospheric glow discharge chambers.

[0020] Preferred uses of the coatings of the substrates coated in accordance with the present invention include lamination adhesives, oxygen and/or moisture barrier for example for food packaging applications and as a component in or on organic light emitting diode devices in, for example, flat panel displays.

[0021] The present invention will now be illustrated in detail with reference to the accompanying drawing, in which Figure 1 shows an embodiment of apparatus according to the present invention.

[0022] The apparatus according to the present invention shown in Figure 1 comprises means for generating an atmospheric pressure plasma discharge (generally designated 10), and an atomiser (generally designated 12) connected to a syringe pump 14 for supplying a coating forming material to the atomiser 12. The means for generating the discharge 10 includes a high voltage 15 kHz ac power supply 20, supplied across two aluminium electrodes 22 and 24 spaced 12mm apart, with the lower live electrode 22 shielded by a glass dielectric plate 26. The atomiser 12 includes a Sono-tek^{*} 8700-120 ultrasonic nozzle 30, and is connected to a Sono-tek^{*} 06-05108 broadband ultrasonic generator 32. The atomiser 12 is seated within the earth electrode 24 on an O-ring 34. The substrate 40 to be coated is placed on the glass dielectric plate 26 between the electrodes 22 and 24.

[0023] The apparatus described hereinabove with reference to Figure 1 was used for all the procedures described hereinafter.

Example 1

[0024] A piece of polyethylene film substrate was ultrasonically washed in a 1:1 mixture of isopropyl alcohol and cyclohexane and was placed on the glass plate. After evacuation of residual gas, the plasma discharge gas was introduced at a flow rate of 1900 sccm and a pressure of 1.02x10⁵ Nm⁻². Two discharge gasses were used, helium and a 99% helium/1% oxygen mixture. After 10 minutes of purging, the syringe pump 14 was switched on and the coating-forming material was allowed to flow at a rate of 3x10⁻⁵ mls⁻¹. Two coating-forming materials were used, octamethylcyclotetrasiloxane (hereinafter referred to as "D₄") and tetramethylcyclotetrasiloxane (hereinafter referred to as "D₄H").

[0025] When the coating-forming material reached the ultrasonic nozzle, the ultrasonic generator was switched on (2.5 W) to initiate atomisation of the coating-forming material, and the atmospheric pressure plasma discharge was ignited by applying 1.5 kV across the electrodes. Deposition of the coating-forming material was allowed to proceed for 10 min (* Sono-tek Corporation, Milton, New York 12547, USA).

utes, following which the substrate was removed and placed under vacuum for 20 minutes to remove any labile material. [0025] The results of the above procedure are shown in Table 1 below. X-ray photoelectron spectroscopic analysis (Kratos ES300) was used to perform elemental analysis of the substrate surface, and a spectrophotometer (Aquila Instruments nkd-6000) was used to determine film thickness. Contact angle measurements were made using video capture apparatus (AST Products VCA2500XE) using sessile 2 μ L droplets of deionised water.

[0026] Gas permeation measurements of the substrate surface were also taken using a mass spectrometer, and the results are shown in Table 2. The Barrier Improvement Factor is calculated as [coated substrate gas permeation]/[reference sample gas permeation].

Table 1

Sample	XPS analysis				Contact Angle (Θ)	Deposition rate (nms $^{-1}$)	Coating thickness (nm)
	%C	%O	%Si	%SiO _x			
D ₄ theory	50	25	25	0	-	-	-
D ₄ 100% He	43.3	29.3	25.8		107.8*	28	279
D ₄ 1% O ₂	25.5	48.5	26.0	74.4	56.4	29	286
D ₄ H theory	33.3	33.3	33.3	0	-	-	-
D ₄ H 100%He	32.5	39.1	28.4		102.3	82	
D ₄ H 1% O ₂	9.2	61.4	29.5	81.5	wets	244	

* clean polyethylene has a contact angle of 105.89

Table 2

Sample	Barrier Improvement Factor
Clean polyethylene	1.0 (by definition)
D ₄ , 100% He	0.9
D ₄ , 1% O ₂	6.8
D ₄ H, 100% He	0.9
D ₄ H, .1% O ₂	4.5

[0027] ATR-FTIR studies of the substrate surfaces showed that ring-opening polymerisation of the D₄ and D₄H coating-forming materials had occurred to form a polysiloxane on the substrate surface. In particular, the ATR-FTIR studies on the latter showed that the polysiloxane coating retained much of the D₄H Si-H functionality.

[0028] NMR studies of a coating prepared as described above on a glass surface showed that the polysiloxane formed on the substrate surface by polymerisation of the D₄ and D₄H coating-forming materials comprised divalent (CH₃)₂SiO_{2/2} units and trivalent CH₃SiO_{3/2} units, i.e. the polysiloxane is resinous.

Example 2

[0029] The method of Example 1 above was repeated using a glass substrate and acrylic acid as the coating-forming material, and helium alone as the discharge gas. The coating was removed from the substrate prior to analysis.

[0030] FTIR and solid state NMR analysis of the coating confirmed that the acrylic acid had polymerised to form polyacrylic acid. Both FTIR and NMR data showed consumption of the unsaturated C=C bond.

Example 3

[0031] The method of Example 2 was repeated, but using nylon and polyethylene substrates.

[0032] An FTIR analysis comparison of the coating with commercially available polyacrylic acid confirmed that the acrylic acid coating-forming material had polymerised to form a polyacrylic acid coating on the substrate surfaces.

[0033] X-ray photoelectron spectroscopic analysis, film thickness analysis, and contact angle measurements were performed per Example 1 above. The results are shown in Table 3 below.

Table 3

	XPS analysis			Contact Angle (θ)	Deposition rate (nms ⁻¹)
	%C	%O	%CO ₂ H		
5	Theory	60.0	40.0	33.3	-
10	Commercial polyacrylic acid	63.3	36.7	29.9	wets
15	Example 3 coating	62.6	37.4	26.4	wets
20					231±95

[0034] Gas transport through the coated polyethylene film was determined by mass spectrometry, and the barrier improvement factor calculated per Example 1 above over an untreated polyethylene substrate and commercially available polyacrylic acid. The results are shown in Table 4 below.

Table 4

Sample	Barrier Improvement Factor
Untreated substrate	1.0 (by definition)
Commercial polyacrylic acid	1.1±0.1
Example 3 coating	7.2±0.9

[0035] A lap shear test was performed on the coated nylon substrates as follows. Two opposing faces of coated nylon substrates were overlapped to create a joint covering 1cm², and the substrates were cured under a 2kg weight at 70°C for 60 minutes. The adhesive strength of each joint was then determined by pulling the substrates apart at a rate of 5mm per minute using a tensiometer (Instron), and recording the maximum load reached prior to failure. The coated substrates withstood a maximum load of 74±11 Ncm⁻² prior to failure. Comparison joints made from uncoated nylon displayed no adhesive properties.

Example 4

[0036] The method of Example 2 was repeated, using a glass substrate and 1H,1H,2H-perfluoro-1-octene (CF₃(CF₂)₅CH=CH₂) as the coating-forming material.

[0037] X-ray photoelectron spectroscopic analysis, FTIR analysis and contact angle measurements (with water and decane) were performed per Example 1 above, and results are shown in Table 5 below. The XPS and FTIR analysis showed that the glass substrate coating was rich in CF₂ and CF₃ and the contact angles for water and decane were determined as per example 1.

Table 5

	XPS analysis			Contact Angle (water) (θ)	Contact Angle (decane) (θ)
	%C	%F	%O		
40	Theory	38.1	61.9	-	-
45	Example 4 coating	38.0	60.0	2.1	118.9±3.0
50					61.1±2.2

[0038] The contact angle measurement results show that the glass substrate has been rendered substantially hydrophobic and oleophobic by the coating.

Claims

- 55 1. A method for forming a coating on a substrate, which method comprises introducing an atomised liquid and/or solid coating-forming material into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom, and exposing the substrate to the atomised coating-forming material under conditions of atmospheric pressure.

- 2. A method according to Claim 1 wherein the coating-forming material is introduced by direct injection.
- 3. A method according to Claim 1 or 2 wherein the coating-forming material is a silicon-containing material.
- 5 4. A method according to Claim 3 wherein the coating-forming material is selected from a dimethylsiloxane, and a siloxane having silicon-hydrogen bonds.
- 10 5. A method according to any preceding Claim wherein the plasma is generated in an oxygen containing atmosphere.
- 6. A method according to Claim 1 or 2 wherein the coating-forming material is an organic or organometallic material.
- 15 7. A method according to Claim 6 wherein the coating-forming material is selected from acrylic acid and a perfluor-olefins.
- 8. A method according to any preceding Claim wherein the substrate comprises metal, ceramic, plastics, woven or non-woven fibres, natural fibres, synthetic fibres, cellulosic material, and powder.
- 10 9. A method according to any preceding Claim wherein the coating increases the adhesive, release, gas barrier, moisture barrier, electrical and thermal conductivity, optical, dielectric, hydrophilic, hydrophobic, and/or oleophobic properties of the substrate.
- 15 10. A method of producing a substrate having a multi-layered coating according to any preceding claim whereby the coating is applied by repeatedly passing said substrate through the atmospheric plasma glow discharge or by passing said substrate through a series of atmospheric glow discharge chambers.
- 20 11. A method according to any one of claims 1 to 4, 6 or 7 wherein the chemical properties of the atomised liquid and/or solid coating forming material are substantially retained in the resulting coating formed.
- 25 12. A method in accordance with any preceding claim wherein the substrate is coated continuously by use of a reel to reel apparatus.
- 30 13. A method in accordance with any preceding claim wherein the substrate is pre-treated by exposure to plasma prior to the introduction of coating forming material.
- 35 14. A method in accordance with any preceding claim wherein the coating formed on the substrate is post treated by exposure to plasma.
- 40 15. A method in accordance with claim 13 or 14 wherein the plasma is applied by way of atmospheric pressure glow discharge.
- 16. A method in accordance with claim 15 wherein an oxygen containing material is added to the plasma.
- 45 17. A method in accordance with claim 16 wherein the oxygen containing materials are selected from the group of oxygen gas and water.
- 18. A method in accordance with claim 1 wherein the coating-forming material consists of monomer materials, and said monomer materials after having been atomised, are co-polymerised by being exposed to an atmospheric pressure plasma discharge.
- 50 19. Apparatus for forming a coating on a substrate under conditions of atmospheric pressure, which apparatus comprises means for generating an atmospheric pressure plasma glow discharge within which, in use, the substrate is placed, an atomiser for providing an atomised liquid and/or solid coating-forming material within the plasma discharge, and means for supplying said coating forming material to the atomiser.
- 55 20. Apparatus in accordance with claim 19 wherein the atomiser is an ultrasonic nozzle.
- 21. Apparatus in accordance with claim 19 or 20 wherein the substrate is fixed to a reel to reel apparatus to enable a continuous coating of the substrate.

22. Use of a coated substrate formed in accordance with the method of any one of claims 1 to 17 as a lamination adhesive, an oxygen and/or moisture barrier or in organic light emitting diode devices.

5 Patentansprüche

1. Ein Verfahren zur Herstellung einer Beschichtung auf einem Trägermaterial, bei dem eine zerstäubte Flüssigkeit bzw. ein beschichtungsherstellendes Material in Festform in eine Plasmaentladung unter atmosphärischem Druck bzw. in einen sich daraus ergebenden ionisierten Gasstrom eingeführt wird, und bei dem das Trägermaterial dem zerstäubten, beschichtungsherstellenden Material unter atmosphärischen Druckbedingungen ausgesetzt wird.
2. Ein Verfahren nach Anspruch 1, bei dem das beschichtungsherstellende Material durch Direkteinspritzung zugeführt wird.
15. 3. Ein Verfahren nach Anspruch 1 oder 2, bei dem das beschichtungsherstellende Material ein silikonhaltiges Material ist.
4. Ein Verfahren nach Anspruch 3, bei dem das beschichtungsherstellende Material aus einem Dimethylsiloxan und einem Siloxan mit Silikon-Wasserstoff-Verbindungen ausgewählt wird.
20. 5. Ein Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Plasma in einer sauerstoffhaltigen Atmosphäre erzeugt wird.
6. Ein Verfahren nach Anspruch 1 oder 2, bei dem das beschichtungsherstellende Material ein organisches oder organisch-metallisches Material ist.
25. 7. Ein Verfahren nach Anspruch 6, bei dem das beschichtungsherstellende Material aus Acrylsäure und einem Perfluoralken ausgewählt wird.
8. Ein Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Trägermaterial aus Metall, Keramik, Plastik, gewebten oder ungewebten Fasern, Naturfasern, synthetischen Fasern, Zellulosestoffen oder aus Pulver hergestellt sein kann.
30. 9. Ein Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Beschichtung die Klebe-, Freisetzung-, Gassperr-, feuchtigkeitsabweisenden, elektrischen und thermalen Leitfähigkeitseigenschaften, sowie die optischen, dielektrischen, hydrophilen, wasserabweisenden bzw. ölabweisenden Eigenschaften des Trägermaterials verbessert.
40. 10. Ein Verfahren zur Herstellung eines Trägermaterials mit mehrlagiger Beschichtung nach einem der vorhergehenden Ansprüche, bei dem die Beschichtung aufgebracht wird, indem das besagte Trägermaterial die atmosphärische Plasmaglimmentladung wiederholt durchläuft, oder eine Reihe von Glimmentladungskammern unter Atmosphärendruck durchläuft.
45. 11. Ein Verfahren nach einem der Ansprüche 1 bis 4, 6 oder 7, bei dem die chemischen Eigenschaften der zerstäubten Flüssigkeit bzw. des Beschichtungsmaterials in Festform ganz wesentlich in der abschließend hergestellten Beschichtung erhalten bleiben.
12. Ein Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Trägermaterial kontinuierlich unter Verwendung einer Bandlaufvorrichtung beschichtet wird.
50. 13. Ein Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Trägermaterial durch Plasmaaussetzung vor der Einbringung des beschichtungsherstellenden Materials behandelt wird.
14. Ein Verfahren nach einem der vorhergehenden Ansprüche, bei dem die auf dem Trägermaterial aufgebrachte Beschichtung durch Plasmaaussetzung nachbehandelt wird.
55. 15. Ein Verfahren nach Anspruch 13 oder 14, bei dem das Plasma unter atmosphärisch beaufschlagter Glimmentladung eingebracht wird.

16. Ein Verfahren nach Anspruch 15, bei dem dem Plasma ein sauerstoffhaltiges Material beigegeben wird.
17. Ein Verfahren nach Anspruch 16, bei dem die sauerstoffhaltigen Materialien aus der Gruppe Sauerstoffgas und Wasser ausgewählt werden.
- 5 18. Ein Verfahren nach Anspruch 1, bei dem das beschichtungsherstellende Material aus Monomermaterialien besteht, wobei diese Monomermaterialien nach ihrer Zerstäubung durch Aussetzung gegenüber einer Plasmaentladung unter Atmosphärendruck co-polymerisiert werden.
- 10 19. Apparat zur Herstellung einer Beschichtung auf einem Trägermaterial unter atmosphärischem Druck, wobei dieser Apparat über eine Vorrichtung verfügt, um eine Plasmaglimmentladung unter Atmosphärendruck zu erzeugen, in die das Trägermaterial bei Anwendung eingeführt wird, des weiteren über einer Zerstäuber zum Erhalt zerstäubter Flüssigkeit bzw. zerstäubten, beschichtungsherstellenden Materials in Festform innerhalb der Plasmaentladung, sowie über eine Vorrichtung, um das besagte beschichtungsherstellende Material in den Zerstäuber einzuführen.
- 15 20. Apparat nach Anspruch 19, bei dem der Zerstäuber eine Ultraschalldüse ist.
21. Apparat nach Anspruch 19 oder 20, bei dem das Trägermaterial an einer Bandlaufvorrichtung befestigt wird, um eine fortlaufende Beschichtung des Trägermaterials zu ermöglichen.
- 20 22. Verwendung eines beschichteten Trägermaterials, das nach dem Verfahren eines der Ansprüche 1 bis 7 als Haftbeschichtung, sauerstoff- bzw. feuchtigkeitsabweisend oder in organischen Leuchtdiodenausführungen hergestellt wurde.
- 25 Revendications
1. Une méthode pour former un revêtement sur un substrat, cette méthode comprend l'introduction d'un liquide atomisé et / ou d'un matériau formant un revêtement solide dans une décharge de plasma à pression atmosphérique et /ou un jet de gaz ionisé résultant de celle-ci, et exposant le substrat au matériau formant un revêtement suivant des conditions de pression atmosphérique.
 2. Une méthode selon la Revendication 1, dans laquelle le matériau formant un revêtement est introduit par injection directe.
 3. Une méthode selon l'une des Revendications 1 ou 2, dans laquelle le matériau formant un revêtement est un matériau contenant de la silicone.
 4. Une méthode selon la Revendication 3, dans laquelle le matériau formant un revêtement est sélectionné à partir de siloxane de diméthyle et d'un siloxane possédant des liaisons silicone hydrogène.
 5. Une méthode selon toute Revendication précédente, dans laquelle le plasma est généré dans une atmosphère contenant de l'oxygène.
 - 45 6. Une méthode selon l'une des Revendications 1 ou 2, dans laquelle le matériau formant un revêtement est un matériau organique ou organo-métallique.
 7. Une méthode selon la Revendication 6, dans laquelle le matériau formant un revêtement est sélectionné à partir d'un acide acrylique et d'un alcène perfluore.
 - 50 8. Une méthode selon toute Revendication précédente, dans laquelle le substrat se compose de métal, céramique, plastiques, fibres tissées ou non tissées, fibres naturelles, fibres synthétiques, matériaux cellulosiques et poudre.
 9. Une méthode suivant toute Revendication précédente, dans laquelle le revêtement augmente les propriétés adhésives, de dégagement, de barrière contre les gaz, de barrière contre l'humidité, de conductibilité électrique et thermique, optiques, diélectriques, hydrophiles, hydrophobes, et / ou oléophobes du substrat.
- 55 10. Une méthode de production d'un substrat possédant un revêtement de plusieurs couches selon toute revendication

- précédente, par laquelle le revêtement est appliqué en passant de façon répétitive ledit substrat à travers une décharge luminescente de plasma à pression atmosphérique ou en passant ledit substrat à travers une série de chambres de décharge luminescente atmosphérique.
- 5 11. Une méthode selon l'une des revendications de 1 à 4, 6 ou 7, dans laquelle les propriétés chimiques du liquide atomisé et / ou du matériau formant un revêtement solide sont en grande partie conservées dans le revêtement résultant formé.
- 10 12. Une méthode selon toute revendication précédente, dans laquelle le substrat est revêtu sans interruption en utilisant un appareil de bobine à bobine.
- 13. Une méthode selon toute revendication précédente, dans laquelle le substrat est prétraité par exposition au plasma avant l'introduction du matériau formant un revêtement.
- 15 14. Une méthode selon toute revendication précédente, dans laquelle le revêtement formé sur le substrat est traité ultérieurement par exposition au plasma.
- 20 15. Une méthode suivant l'une des revendications 13 ou 14, dans laquelle le plasma est appliquée par décharge luminescente à pression atmosphérique.
- 25 16. Une méthode selon la revendication 15, dans laquelle un matériau contenant de l'oxygène est ajouté au plasma.
- 17. Une méthode selon la revendication 16, dans laquelle les matériaux contenant de l'oxygène sont sélectionnés à partir du groupe d'oxygène et d'eau.
- 25 18. Une méthode selon la revendication 1, dans laquelle le matériau formant un revêtement se compose de matériaux monomères et ces matériaux monomères, après avoir été atomisés, sont co-polymérisés en étant exposés à une décharge de plasma à pression atmosphérique
- 30 19. Un appareil pour former un revêtement sur un substrat suivant des conditions de pression atmosphérique, cet appareil comprend des façons de générer une décharge luminescente à pression atmosphérique dans lesquelles on place le substrat, lors de l'utilisation, un atomiseur pour fournir un liquide atomisé et /ou un matériau formant un revêtement solide à l'intérieur de la décharge de plasma, et des moyens de fournir ledit matériau formant un revêtement vers l'atomiseur.
- 35 20. Un appareil selon la revendication 19, dans lequel l'atomiseur est un embout ultrasonique.
- 21. Un appareil selon l'une des revendications 19 ou 20, dans lequel le substrat est fixé à un appareil de bobine à bobine pour permettre un revêtement continu du substrat.
- 40 22. L'utilisation d'un substrat revêtu, selon la méthode de toute revendication de 1 à 17, en tant qu'adhésif de laminage, barrière contre l'oxygène et / ou contre l'humidité ou dans des appareils à diodes électroluminescentes organiques.

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FIG. 1

